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Photoluminescent Metal–Organic Polymer Constructed from Trimetallic Clusters and Mixed Carboxylates

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The solvothermal reaction of zinc acetate dihydrate with a mixture of benzene-1,4-dicarboxylic acid (H_2BDC) and benzene-1,3,5-tricarboxylic acid (H_3BTC) in a solution containing *N*,*N′*-dimethylformamide (DMF), absolute ethanol, and chlorobenzene gave rise to a metal–organic polymer, $Zn_3{\cdot}BDC{\cdot}2BTC{\cdot}2NH(CH_3)_2{\cdot}2NH_2(CH_3)_2$. The structure of this polymer possesses a unique three-dimensional framework with tri-zinc clusters, and BDC and BTC units colinking the clusters. Moreover, this metal–organic polymer exhibits strong photoluminescence at room temperature, and the main emission band is at about 430 nm ($\lambda_{ex} = 325$ nm). Crystal data for this compound ($C_{17}H_{20}N_2O_8Zn_{1.5}$): monoclinic, space group $P2_1/n$, cell dimensions $a = 11.6171(3)$ Å, $b = 14.2456(4)$ Å, $c = 12.6426(3)$ Å, $\beta = 107.030(2)°$, $V = 2000.51(9)$ Å^3, and $Z = 4$.

Metal–organic polymers built up from metallic clusters and multi-carboxylate building blocks have been extensively studied in recent years, due to their interesting molecular topologies and crystal packing motifs[1] along with potential applications as functional materials.[2] The metallic clusters in these polymers exhibit a variety of coordination advantages and may introduce intriguing magnetic[3] and spectroscopic properties[4] to the polymeric frameworks. On the other hand, the multi-carboxylate building blocks with special configurations, such as benzene-1,4-dicarboxylic acid (H_2BDC) with a 180° angle and benzene-1,3,5-tricarboxylic acid (H_3BTC) with a 120° angle between two carboxylic groups, can yield desired networks[5–7] in metal–organic polymers and tune their chemical selectivity[8] or chirality.[7c,9]

As individual organic linkers, H_2BDC[5,6] and H_3BTC[7] have been the versatile ligands with good binding ability as manifested by the formation of 1D, 2D, and 3D polymeric structure systems from these two molecules. Although a few polymers constructed by H_2BDC or H_3BTC in the presence of an auxiliary amine ligand have been synthesized,[10] no metal–organic polymer with two different carboxylate ligands has appeared in the literature. In our experiment, we incorporate H_2BDC and H_3BTC into the solvothermal system including zinc ions to produce a new metal–organic polymer, $Zn_3{\cdot}BDC{\cdot}2BTC{\cdot}2NH(CH_3)_2{\cdot}2NH_2(CH_3)_2$. To our knowledge, this is the first example in which two different multicarboxylates as organic linkers are incorporated into one metal–organic polymer.

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The solvothermal reaction of zinc acetate dihydrate (0.066 g, 0.6 mmol) with H_2BDC (0.050 g, 0.3 mmol) and H_3BTC (0.042 g, 0.2 mmol) in a mixture of *N*,*N′*-dimethylformamide (DMF) (3 mL), absolute ethanol (2 mL), and chlorobenzene (3 mL) was performed at 160 °C for 72 h to give colorless crystals of the polymer with ca. 62% yield. The IR spectrum reveals two strong bands of the carboxylic groups at 1622 and 1586 cm^{-1} for the asymmetric vibrations and at 1439 and 1370 cm^{-1} for the symmetric vibrations. The absence of the characteristic bands at around 1700 cm^{-1} attributed to the protonated carboxylic groups indicates the complete deprotonation of BDC and BTC ligands upon reaction with Zn ions. Thermogravimetric analysis (TGA) shows that the first weight loss of 9.32% from 140 to 240 °C corresponds to the loss of one dimethylamine molecule (calculated: 9.42%). The protonated dimethylamine cations, BTC and BDC units are lost in four steps at 328 (7.35%), 372 (8.52%), 438 (16.68%), and 600 °C (33.38%). Powder X-ray diffraction shows that the polymer finally transforms to ZnO after being heated at 600 °C. The total weight loss of this polymer is about 75.25%, in accordance with the calculated value on the basis of the single crystal structure formula (74.55%). Phase purity of the polymer is sustained by its powder diffraction pattern, which is consistent with the simulated one from the X-ray single crystal diffraction data.

X-ray single crystal diffraction analysis[11] on a crystal obtained from the reaction product reveals that the structure of this polymer possesses a three-dimensional framework composed of the trimetallic cluster consisting of two four-coordinate and one six-coordinate zinc centers (Figure 1). The three zinc centers, with an inversion center on Zn1, are bridged through two symmetry-inequivalent BTC units and one BDC unit. It is interesting that the carboxylate oxygens are tightly bonded to Zn2 (Zn2−O2 = 1.964(2) Å, Zn2−O4 = 1.934(2) Å, Zn2−O5 = 1.9466(18) Å and Zn2−O8 = 1.942(2) Å), while they are weakly coordinated to Zn1 (Zn1−O1 = 2.1169(18) Å, Zn1−O3 = 2.0485(17) Å, and Zn1−O7 = 2.1592(18) Å).

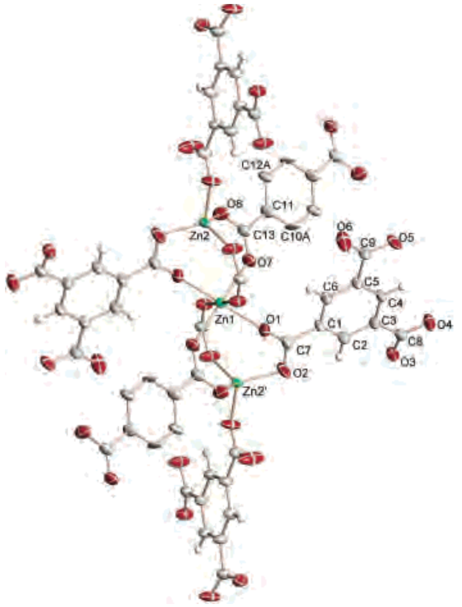

Figure 1. Tri-zinc cluster including the asymmetric unit present in the polymer is represented by thermal ellipsoids drawn to encompass 50% of their electron density. (The split positions [C10B, C10C, C12B, and C12C] of the BDC unit and the two BTC units except for their carboxylate groups are not shown for clarity).

In this crystal, the trimetallic clusters are polymerized through the BTC units to yield one-dimensional straight rectangular channels running along the [001] direction. These rectangular channels are further subdivided by the BDC units (Figure 2a). There also exist one-dimensional channels (Figure 2b) along the [−322] direction. Furthermore, the results of X-ray single-crystal diffraction analysis, IR spectrum analysis, X-ray photoelectron spectroscopy (XPS), and elemental analysis[11b] indicate that there are one disordered protonated dimethylamine cation and one disordered dimethylamine molecule. The N−H absorption vibration for dimethylamine molecules appears at ca. 3500 cm^{-1}, and the XPS N_{1s} peaks of deprotonated and protonated dimethylamines are observed at 398.8 and 401.9 eV, respectively. There exist N−H···O hydrogen bonds between the protonated dimethylamine cations and the oxygen atoms of carboxylate groups. The observed distances of the N atom to two carboxylate oxygens are 2.718(4) and 3.196(4) Å for N1−H2(N)···O6 and N1−H2(N)···O8, respectively.

The diffuse reflectance UV−vis spectra for H_2BDC, H_3BTC, and the as-synthesized polymer show different absorption features (Figure 3). There are essentially two bands for H_2BDC and H_3BTC, and the longer and shorter wavelength absorptions correspond to the intraligand $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions, respectively.[13] In comparison with the two bands for H_2BDC and H_3BTC, the shorter wavelength band for the polymer remains the same in energy, whereas the longer wavelength band, appearing as a shoulder in the spectrum, shifts toward higher energy. This hypsochromic shift must be related to the coordination of Zn^{2+} to the BDC and BTC molecules, and it may arise from the same $n \rightarrow \pi^*$ transition with the n orbitals (HOMO located on the O atoms

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(11) (a) Crystallographic data for the polymer were recorded at room temperature on a Bruker-AXS Smart CCD diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares techniques against F^2 using the SHELXTL-NT5.1 package.[12] Non-hydrogen atoms were refined anisotropically, of which C10 and C12 in the phenylene of BDC molecules and C14, C15, C17, and N2 in the dimethylamines appeared to be disordered. This disorder could be resolved by using split positions (C10A−C10C, C12A−C12C, C14A−C14D, C15A−C15D, C17A−C17B, and N2A−N2D). The hydrogen atoms in the phenylene groups of BTC molecules were generated with idealized geometries. The bonding to nitrogen atoms of protonated dimethylamines was found in the electron density map and refined isotropically. All other hydrogen atoms were not included. (b) Crystal data: size = 0.36 × 0.20 × 0.16 mm^3; formula, $C_{17}H_{20}N_2O_8Zn_{1.5}$; MW, 478.40; monoclinic, space group $P2_1/n$; cell dimensions $a = 11.6171(3)$ Å, $b = 14.2456(4)$ Å, $c = 12.6426(3)$ Å, $\beta = 107.030(2)°$, $V = 2000.51(9)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.588$ g·cm^{-3}; $\mu = 1.859$ mm^{-1}; $T = 293(2)$ K. A total of 16341 reflections were collected, of which 5826 were independent reflections [R(int) = 0.0467]. Final R indices [$I > 2\sigma(I)$]: R1 = 0.0385, wR2 = 0.0810. R indices (all data): R1 = 0.0735, wR2 = 0.0900, GOF = 0.937. Maximum and minimum residual electron density are 0.567 and −0.406 e·Å^{-3}. Elemental Anal. Calcd: C, 42.72; H, 4.19; N, 5.86. Found: C, 42.06; H, 3.68; N, 5.84.

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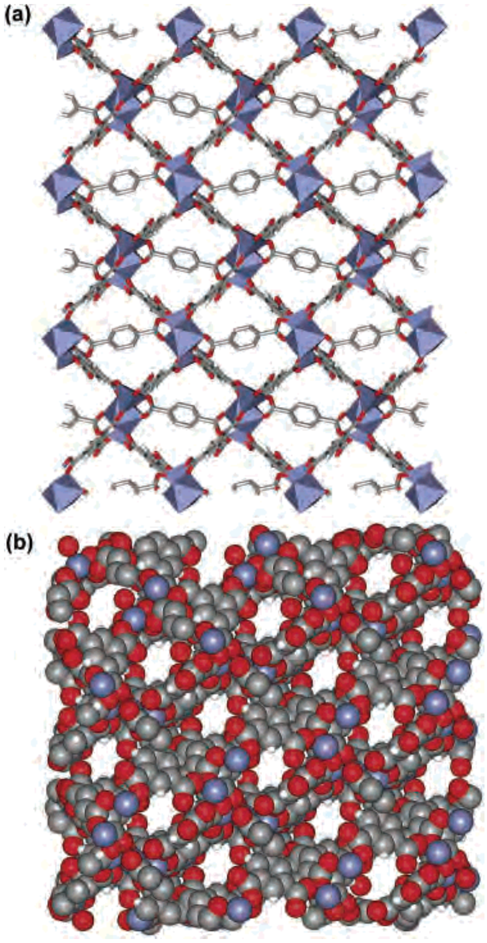

Figure 2. Structure of the polymer: (a) the subdivision of the 1D rectangular channels by BDC units viewed along the [001] direction and (b) the 1D channels viewed along the [$\bar{3}$22] direction.

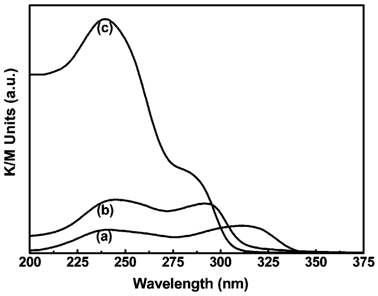

Figure 3. dDiffuse reflectance UV−vis spectra of (a) H_2BDC, (b) H_3-BTC, and (c) the as-synthesized polymer at room temperature.

of the carboxylate groups) being perturbed by the Zn^{2+} cations of the polymer. It is noted that the absorption intensity (in Kubelka−Munk units) of the polymer is markedly higher than that for either of the ligands. This significant increase in absorption intensity is attributable to the involvement of charge-transfer transitions from the O atoms of the ligands to the empty 4s orbitals of the Zn^{2+} ions. Both H_2BDC and H_3BTC show photoluminescence (Figure 4). The main emission peak for both compounds is located at the same position, but the strongest excitation peak for H_2BDC is at 350 nm and that for H_3BTC is 334 nm. The emission bands for these two ligands are attributable to the $\pi^* \rightarrow n$ transitions. Interestingly, the emission spectrum for the metal−organic polymer shows a main peak at 430 nm with a shoulder at about 370 nm. A similar emission band at about 430 nm has also been observed previously for other zinc−organic polymer compounds[14] with either photoluminescent or nonphotoluminescent ligands. Therefore, this emission may not be related to the $\pi^* \rightarrow n$ transition of the ligands but simply arises from the charge-transfer transition.[6b,7e,14] However, the shoulder peak of the emission spectrum at 370 nm is probably due to the $\pi^* \rightarrow n$ transition because a shoulder emission peak at 370 nm also appears for the ligand H_3BTC (Figure 4b). The strongest excitation peak for the polymer is at 325 nm, a higher energy than those for the H_2BDC and H_3BTC excitation peaks. This excitation peak of the polymer is coincident, in peak position, with the threshold of the UV−vis absorption band of the polymer. We have also recorded the surface photovoltaic spectrum for the polymer compound, and it is found that the compound shows a weak photovoltaic effect, suggesting that the photoexcited electrons are not completely localized on the zinc atoms or on the ligands.

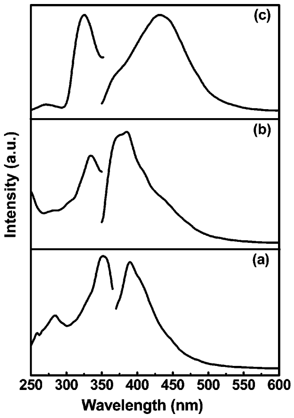

Figure 4. Solid state photoluminescent spectra of (a) H_2BDC, (b) H_3-BTC, and (c) the as-synthesized polymer at room temperature.

In summary, we have demonstrated the synthesis of a photoluminescent metal−organic polymer through the combined use of H_2BDC and H_3BTC. In contrast to those previously reported structures constructed from individual H_2BDC[5,6] or H_3BTC,[7] the fabrication of a unique framework through mixed H_2BDC and H_3BTC in our polymer can effectively increase the structural diversity. Furthermore, the polymer can be excited directly and emit strong luminescence at room temperature.

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Supporting Information Available: Experimental procedures, FTIR curve, TGA curve, powder diffraction patterns for the polymer and ZnO, surface photovoltage spectrum, six tables, two figures, and X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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